



Characterization of Rh/Al₂O₃ catalysts after calcination at high temperatures under oxidizing conditions by luminescence spectroscopy and catalytic hydrogenolysis

Vladimir O. Stoyanovskii*, Alexei A. Vedyagin, Galina I. Aleshina, Alexander M. Volodin, Alexander S. Noskov

Boriskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Pr.Akademika Lavrentieva, 5, Novosibirsk, 630090, Russia

ARTICLE INFO

Article history:

Received 4 December 2008

Received in revised form 20 February 2009

Accepted 3 March 2009

Available online 13 March 2009

Keywords:

Luminescence

Rhodium catalyst

Rh/Al₂O₃

Ethane hydrogenolysis

ABSTRACT

Rhodium/alumina catalysts with Rh loadings of 0.01–0.5 wt.% with substantially different thermal stability of supports with respect to phase transformation to corundum were studied. It was shown that the stability of alumina support with respect to its transformations to corundum is one of the important factors accounting for irreversible deactivation of Rh/Al₂O₃ catalysts. We used laser-induced luminescence (LIL) of Cr³⁺ impurity and Rh³⁺ in α -Al₂O₃ and XRD for studying catalysts with different calcination temperatures. Catalytic ethane hydrogenolysis was used as a test for Rh loading on the catalyst surface. This method reliably detects Rh ions on the surface starting from concentrations as low as 0.01%. The results of LIL spectroscopy indicated that in all cases Rh³⁺ ions were incorporated in the bulk of the newly formed α -Al₂O₃ phase, and quite possible can initiate the formation of the corundum phase in catalysts with high-thermal stability.

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1. Introduction

Three-way catalysts (TWC) were conventionally used in the emission control of gasoline vehicles. TWC have the advantage of performing the oxidation of carbon monoxide (CO), hydrocarbons (HC) and the reduction of nitrogen oxides (NO_x) simultaneously [1]. Noble metals are usually used as the active phase in TWC. Pd catalysts are especially attractive since Pd is by far the cheapest noble metal in the market and has better selectivity and activity for hydrocarbons [2]. Rhodium, the other essential constituent of three-way catalysts, is widely recognized as the most efficient catalyst for promoting the reduction of NO to N₂. The TWC performance in the emission control can be affected by operating the catalyst at elevated temperatures (>600 °C) [3]. It is well known that commercial catalysts lose their activity (deactivation phenomenon) as a result of various changes in their structure and chemical state of the surface [4–6]. TWC deactivation can be categorized into three main groups: chemical [4], thermal [7–9], and mechanical. Chemical deactivation is considered to be the most complex of the three processes. Better understanding of the

deactivation mode is needed to devise the means for preventing it, and thus improve the stability of the catalysts.

The diffusion of Rh ions from the support surface into its bulk during calcination of Rh/Al₂O₃ catalysts in an oxidizing environment is well known and has been repeatedly discussed in the literature [10–17]. Based on the available data, these processes effectively proceed at temperatures above 800 °C. An opposite phenomenon is also reported in the literature. The follow-up calcination of the catalysts in a reducing environment (H₂) leads to the Rh return to the surface [10,11], in some cases even increasing the activity of the catalyst in CO oxidation [10].

Most of the studies performed to date were devoted to the catalysts containing sufficiently high concentrations of supported Rh (>0.5 wt.%). At the same time, of considerable interest for practical application are also catalysts containing significantly lower concentrations of supported Rh. Such catalysts operate at high temperatures (up to 1000–1050 °C). Therefore, it was extremely important to study their transformations in this temperature range. Under such conditions, the diffusion of the supported metal is accompanied by the phase transformations of the support leading to the corundum (α -Al₂O₃) formation.

The degree of alumina conversion to the corundum phase largely depends on the presence of chemical impurities and modifiers in the Al₂O₃ support and its treatments. It seems quite natural that at such temperatures Rh ions can be incorporated into α -Al₂O₃ particles. It is very likely that this process is irreversible

* Corresponding author.

E-mail addresses: Stoyanovskii@catanalysis.ru, stoyanovsky@gmail.com (V.O. Stoyanovskii).

because diffusion of ions in corundum at such temperatures is negligible. To the best of our knowledge, there is no information in the literature on the possible role of such processes in deactivation of Rh/Al₂O₃ catalysts. Most likely, this is caused by the problems with detection of Rh³⁺ ions in corundum in low concentrations by traditional physicochemical and catalytic techniques. In the meantime, the application of optical methods, first of all luminescence, is extremely effective for detecting impurity Cr³⁺ ions as well as specially added Rh³⁺ ions in corundum. Laser-induced luminescence (LIL) makes it possible to use natural concentrations of chromium ions 10^{−3} to 10^{−2} wt.% for investigation of the formation of θ -Al₂O₃ and α -Al₂O₃ phases at the earliest stages at conversion degrees 10^{−4}–0.5% [18]. In this range the sensitivity of the XRD method is insufficient, whereas LIL can selectively detect Rh³⁺ ions in α -Al₂O₃ [22].

The current study was devoted to investigation of Rh/Al₂O₃ catalysts containing 0.01–0.5 wt.% Rh after calcination under oxidizing conditions. Catalytic ethane hydrogenolysis was used as a test reaction for the amount of Rh on the catalyst surface. This reaction can be used to detect Rh atoms on the surface accessible to the molecules of the gas phase starting from 0.01% concentrations.

Special attention was paid to incorporation of Rh ions into α -Al₂O₃ crystallites formed in the catalyst and the effect of Rh on the formation of α -Al₂O₃ by LIL spectroscopy.

2. Experimental

Incipient wetness impregnation method was used for the catalyst preparation. RhCl₃·4H₂O (Merck) and γ -Al₂O₃ (Al-1; Condea, SSA = 205 m²/g) were used as starting materials. Prior to the impregnation, aluminum oxide extrudates were crushed, sieved to particle size of 0.1–0.5 mm and calcined at 700 °C for 12 h (γ -Al₂O₃ with SSA = 188 m²/g). Different concentrations of rhodium chloride in the impregnation solution were used to obtain 0.01–0.5 wt.% Rh loadings. An aqueous solution of rhodium chloride was poured on granular support at room temperature. After impregnation the samples were dried in air at room temperature overnight. Then, the samples were dried at 110 °C for 12 h, heated in air to 630 °C at 2 °C/min rate and kept at 630 °C for 12 h. The final calcination was carried out in air at 830 °C (12 h) and 1000 °C (24 h).

The X-ray diffraction (XRD) analysis of samples was performed on HZG-4 diffractometer (Germany) using Co K α radiation. Diffraction patterns from the samples were taken by scanning the $2\theta = 20$ –75° range with 0.05° increments and a count time of 10–20 s per point. Quantitative contents of γ -, δ -, and α -Al₂O₃ were evaluated from calibration plots for mechanical mixtures, containing preset proportions of these pure phases as references. The calibration plot for each mixture series was based on intensity ratios for certain closely spaced reflections from different phases.

The aluminum oxide precursor Al-1 used in the study had high-thermal stability with respect to conversion to corundum. After calcination in air at 1000 °C for 24 h the α -Al₂O₃ concentration was below the XRD sensitivity (Fig. 1). According to the LIL spectra of impurity Cr³⁺ ions registered after excitation with wavelength $\lambda_{\text{ex}} = 514.5$ nm, the α -Al₂O₃ concentration was 0.2–0.3% and that of θ -Al₂O₃ was 0.6–1.0%. The initial support calcined in air at 1200 °C (12 h) was used for relative calibration of the LIL method in determination of α -Al₂O₃ concentration. In some experiments with LIL we used another commercial alumina support Al-2 (IKT-27-20, Angarsk, SSA = 180 m²/g). The degree of its conversion to corundum under the same conditions was much higher (up to 10%, Fig. 1). The Rh deposition method and thermal treatment of the catalysts were the same as described above.

The electronic diffuse reflectance spectra were measured on a UV–vis 4501 instrument (Shimadzu, Japan).

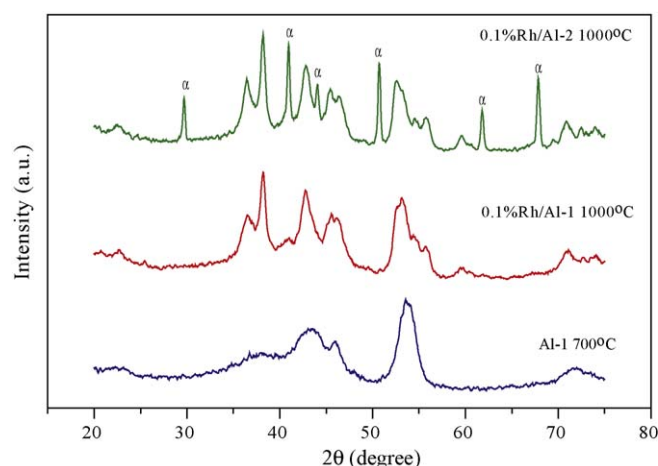


Fig. 1. X-ray diffraction patterns of the alumina support Al₂O₃ (Al-1) 700 °C and catalysts 0.1% Rh/Al-1, 0.1% Rh/Al-2 after calcination at 1000 °C.

2.1. Ethane hydrogenolysis experiments

The surface concentration of rhodium was determined using ethane hydrogenolysis as a test reaction. This reaction takes place only on metals. This fact explains the need in preliminary catalyst reduction in hydrogen flow. The activity of the catalysts correlates with the specific surface area of rhodium metal that is proportional to its surface concentration. The method is sensitive even at very low-rhodium concentrations. The initial reaction rate and the light-off temperature are usually used as measures of the catalytic activity. The higher the concentration of finely dispersed rhodium metal, the lower the light-off temperature and the higher the reaction rate, resulting in a shaper growth of the light-off curve. Rhodium catalysts are active in this reaction between 200 and 400 °C. So, this was the temperature range used in our experiments.

The experimental method was based on the work by Sinfelt and Yates [23]. Fresh catalyst (0.25–0.5 mm fraction, 100 mg loading) was reduced in H₂ flow at 500 °C. Then the reactor was cooled in the hydrogen flow to the reaction temperature. Afterwards, the helium flow was mixed with hydrogen, and the H₂/He mixture was passed through the reactor for some time until the system reached a steady state. At this point, ethane was added to the flow. The ethane flow was passed for a short period of time, usually for 3 min. Then, a probe was taken for chromatographic analysis, and the hydrocarbon flow was stopped. For 10 min of the chromatographic analysis the sample was subjected to the H₂/He mixture flow. This was necessary to regenerate the initial state of the catalyst. This procedure was repeated for five times at each temperature in the studied temperature range with a 25 °C step.

Only experimental points with ethane conversion to methane by hydrogenolysis no more than 10% were used in subsequent calculations. The hydrogenolysis reaction rate (normalized to 1 g Rh) was determined as follows:

$$r = \left(\frac{F}{W} \right) X$$

Here, F is the ethane flow rate (mol/h), W is the Rh mass in the sample (g), and X is the ethane conversion.

2.2. Laser-induced luminescence (LIL) spectroscopy

The measurements were carried out using a spectroscopic bench described earlier [19]. Luminescence was excited with an N₂ laser (wavelength 337.1 nm, pulse duration $\tau_p = 10$ ns; pulse

energy 16 μJ , $F = 100\text{ Hz}$). The beam was focused on the surface of a powder sample placed in a quartz cell. The average radiation power density on the sample surface could be varied between 0.01 and 25 mW/cm^2 using a calibrated radiation attenuator. LIL radiation was focused at the entrance slit of an MDR-12 monochromator (LOMO) and an LN/CCD-1100PF/UV (Princeton Instruments) spectroscopic camera.

3. Results and discussion

3.1. Ethane hydrogenolysis

First, we studied a series of model $\text{Rh}/\text{Al}_2\text{O}_3$ (Al-1) catalysts where the rhodium concentration was varied from 10,000 to 100 ppm. The light-off curves of these samples calcined at 630 °C are shown in Fig. 2. The decrease of the rhodium concentration clearly shifts the curves to higher temperatures. The difference in the light-off curve position for the samples with 10,000–100 ppm Rh is 130 °C.

At the next step $\text{Rh}/\text{Al}_2\text{O}_3$ (Al-1) samples were additionally calcined at 830 and 1000 °C. The results of the catalytic tests for the catalyst with Rh concentration 2000 ppm are presented in Fig. 3. The high-temperature treatment substantially decreased the catalytic activity. Even after treatment at 830 °C the light-off curve was shifted to higher temperatures by 55 °C. Only 198 ppm Rh was left on the surface after such treatment (Table 1). This is 9.9% of its initial concentration. Further increase of the calcination temperature led to some additional decrease of the catalytic activity. The rhodium concentration after calcination at 1000 °C was estimated to be 169 ppm, which is 8.5% of the initial concentration.

The obtained results led us to several important conclusions. First, the used catalytic method can be used at Rh concentrations as low as 100 ppm. Second, the thermal treatment at high temperature leads to active Rh migration from the surface, presumably, into the support. As a result, the Rh surface concentration decreases by more than an order of magnitude. Third, the critical pretreatment temperature is about 800 °C. The most significant activity drop is observed at this temperature. Further increase of the calcination temperature has a minor effect on the surface rhodium concentration.

It is natural to assume that all rhodium ions that disappeared from the surface moved to the subsurface region and the bulk of the alumina particles. According to the literature data, this process is largely reversible at 800–900 °C [10,11]. This means that in this temperature range the mobility of Rh^{3+} ions in the low-

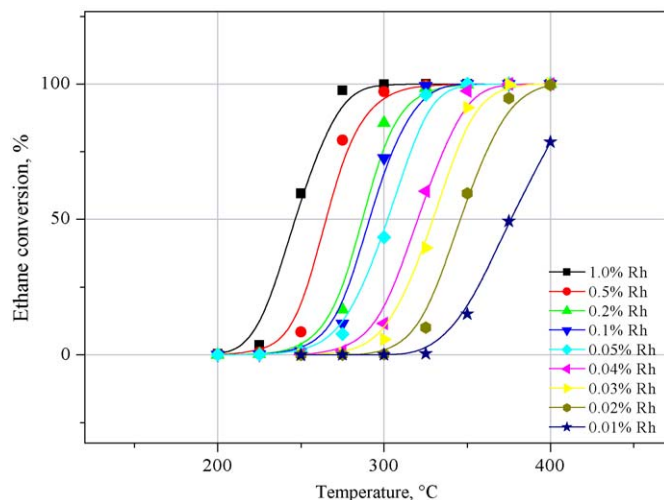


Fig. 2. Light-off curves for the samples with different Rh loading.

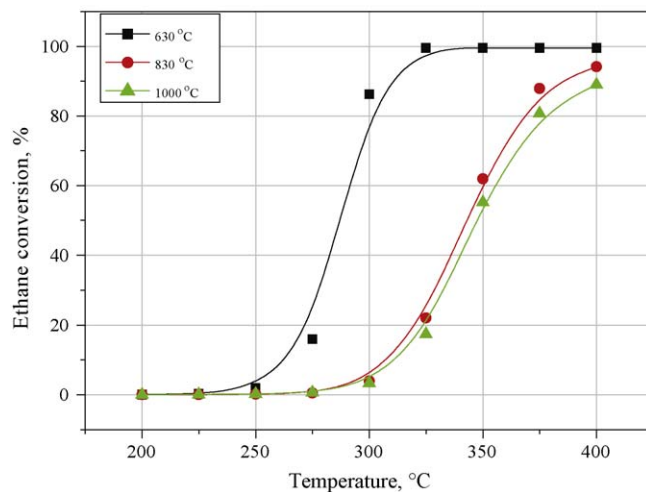


Fig. 3. Light-off curves for the sample 0.2% Rh/Al-1 pretreated at different temperatures.

Table 1

Migration of Rh from the surface during high-temperature pretreatment of $\text{Rh}/\text{Al}_2\text{O}_3$ (Al-1).

No.	Pretreatment temperature (°C)	Surface Rh concentration (ppm)	Amount of Rh left on the surface (%)
1	630	2000	(100)
2	830	198	9.9
3	1000	169	8.5

temperature alumina phases is sufficient to cause their diffusion due to the concentration gradient. Supposedly, sufficiently long treatment of the catalysts at this temperature in oxidizing environment will result in a uniform distribution of Rh ions in alumina particles. This should be true for the catalysts calcined at 1000 °C as well.

3.2. LIL studies

Rh^{3+} ($4d^6$) ions occupying low-spin octahedral positions in $\alpha\text{-Al}_2\text{O}_3$ structure are characterized by a phosphorescence band at 670 nm [22] with typical decay time $\tau \sim 0.6\text{ ms}$ ($T = 300\text{ K}$). The excitation spectrum consists of two well-resolved bands at 390 nm ($25,400\text{ cm}^{-1}$) and 320 nm ($31,200\text{ cm}^{-1}$) corresponding to allowed transitions $^1A_{1g} \rightarrow ^1T_{1g}$, $^1T_{2g}$ and a charge transfer band with the edge at 200 nm. This spectrum is in good agreement with UV–vis diffuse reflectance spectrum of $\text{Rh}^{3+}/\alpha\text{-Al}_2\text{O}_3$ (Al-1, 0.1% Rh, 1200 °C, Fig. 4).

The diffuse reflectance spectra are sensitive to changes of the state of Rh ions during the high-temperature treatment in air (Fig. 5(a)). As rhodium leaves the surface, the intensity of the $^1T_{1g}$ band decreases due to the decrease of the extinction coefficient caused by the decoration of Rh^{3+} ions with the support. The band also shifts from $22,900\text{ cm}^{-1}$ for the surface $\text{Rh}^{3+}/\gamma\text{-Al}_2\text{O}_3$ complexes in the catalyst calcined at 630 °C to $25,125\text{ cm}^{-1}$ for bulk Rh^{3+} ions in corundum in the catalyst calcined at 1200 °C.

Note that the excitation wavelength $\lambda_{\text{ex}} = 337.1\text{ nm}$ of N_2 laser corresponds to $^1T_{1g}$ band of $\text{Rh}^{3+}/\alpha\text{-Al}_2\text{O}_3$. Its absorption intensity linearly grows with the amount of introduced Rh (Fig. 5(b)). To determine if the luminescence sites typical for $\text{Rh}^{3+}/\alpha\text{-Al}_2\text{O}_3$ catalysts can be formed under our conditions, we studied two series of $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts supported in a thermally stable support Al-1 and Al-2 support with low-thermal stability. The latter was partially converted to corundum after calcination at 1000 °C.

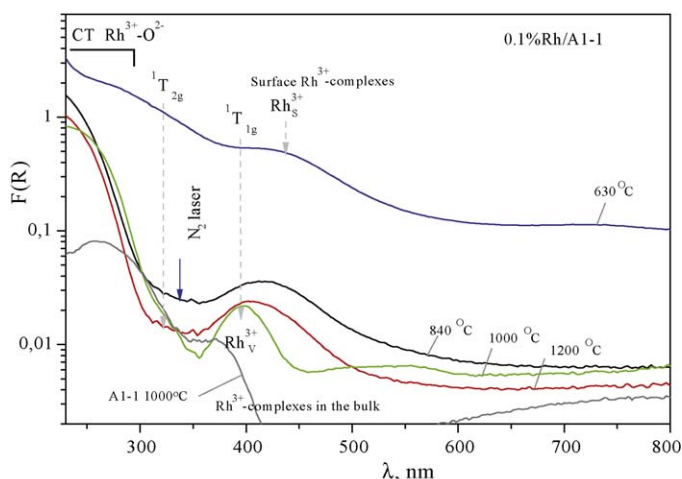


Fig. 4. Diffuse reflectance UV-vis spectra of 0.1% Rh/Al-1 and Al-1 support after calcination at 630–1200 °C. The arrows mark the lines corresponding to transitions $^1A_{1g} \rightarrow ^1T_{1g}$, $^1T_{2g}$ for $Rh^{3+}/\alpha-Al_2O_3$, and relative position of excitation wavelength $\lambda_{ex} = 337.1$ nm of N_2 laser.

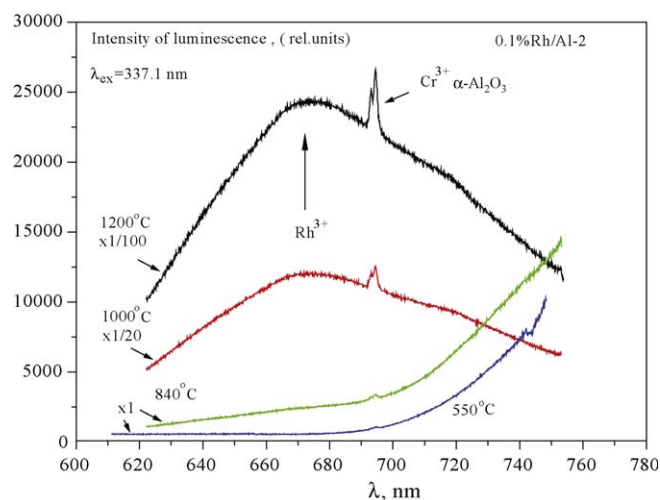


Fig. 6. LIL spectra of 0.1% Rh/Al-2 under excitation wavelength $\lambda_{ex} = 337.1$ nm calcined at different temperatures.

Fig. 6 presents typical luminescence spectra of 0.1% Rh/Al-2 catalyst calcined at different temperatures under excitation with wavelength $\lambda_{ex} = 337.1$ nm. The calcination at 1000 and 1200 °C led to the appearance of an intense band in the LIL spectra at $\lambda = 670$ –680 nm typical for Rh^{3+} ions in $\alpha-Al_2O_3$. In addition to this band, the calcination at high temperatures also resulted in the appearance of an intense doublet R_{α} corresponding to impurity Cr^{3+} ions in corundum. However, in this case the mechanism of luminescence excitation of impurity Cr^{3+} ions in $\alpha-Al_2O_3$ is substantially different from the case when luminescence is excited in the range of their absorption $^4A_2 \rightarrow ^4T_2$ band at wavelength $\lambda_{ex} = 514.5$ nm. First of all, the R_{α} doublet mentioned above was not observed for pure Al-1 samples not doped with Rh that were calcined at 1000–1200 °C. According to both XRD and LIL ($\lambda_{ex} = 514.5$ nm) data, the concentration of $\alpha-Al_2O_3$ phase in such samples varied from 0.2 to 100% (0% Rh/Al-1, 1000 °C, Fig. 7). The doublet observed in the luminescence spectra at 675–678.6 nm that was weakly resolved at room temperature corresponds to

impurity Mn^{4+} ions in $\alpha-Al_2O_3$ [20]. Second, no R_0 doublets of Cr^{3+} ions corresponding to $\theta-Al_2O_3$ phase, which was present in Rh/Al-1 1000 °C sample in 0.6–1.0% concentration, were observed in the registered luminescence spectra of both Rh/Al-2 samples and Rh/Al-1 samples calcined at 830 and 1000 °C after excitation with wavelength $\lambda_{ex} = 337.1$ nm. Taking into account the overlapping of the bands corresponding to $^1T_{2g} Rh^{3+}/\alpha-Al_2O_3$ and $^4T_1 Cr^{3+}/\alpha-Al_2O_3$ energy levels, this fact suggests that nonradiative fluorescence resonance energy transfer (FRET) [21] from donor Rh^{3+} ions in $\alpha-Al_2O_3$ to acceptor Cr^{3+} ions in $\alpha-Al_2O_3$ is possible in this case. Typical distances between the donor-acceptor ion pair for this energy transfer mechanism are less than 8 nm.

Thus, in common case, the luminescence intensity of R_{α} line of Cr^{3+} ions in Rh/Al $_2$ O $_3$ samples after excitation with wavelength $\lambda_{ex} = 337.1$ nm does not reflect the total corundum concentration in the sample. It rather correlates with the concentration of corundum where Rh^{3+} and Cr^{3+} ions are located close to each other ($r < 8$ nm). If the concentration of Rh uniformly distributed in alumina exceeds 0.1 wt.% (Al-1, 1000 °C with SSA = 120 m 2 /g, $d = 13$ nm), typical distances between isolated Rh^{3+} ions become less than 3 nm. In this case the luminescence intensity of acceptor

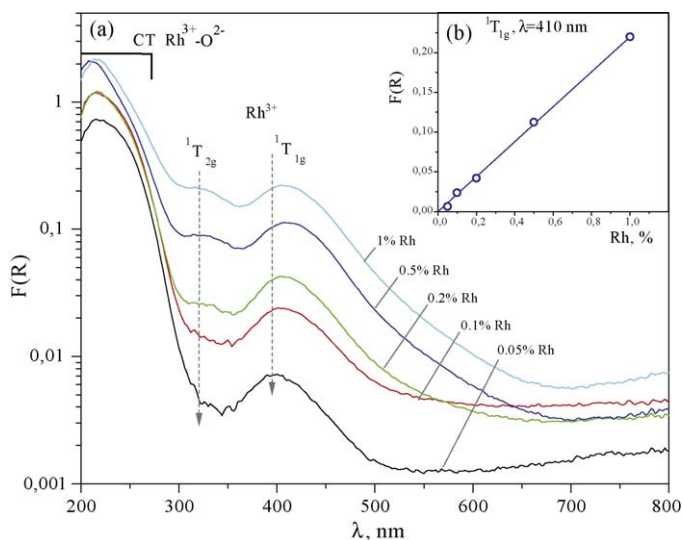


Fig. 5. (a) DR UV-vis spectra of catalysts supported on Al-2 with different Rh concentrations after calcination at 1000 °C. The arrows mark the lines corresponding to transitions $^1A_{1g} \rightarrow ^1T_{1g}$, $^1T_{2g}$ for $Rh^{3+}/\alpha-Al_2O_3$. (b) Dependence of the absorption intensity in the region corresponding to the $^1T_{1g}$ band in the DR UV-vis spectra of Rh/Al-2 catalysts calcined at 1000 °C on the Rh concentration.

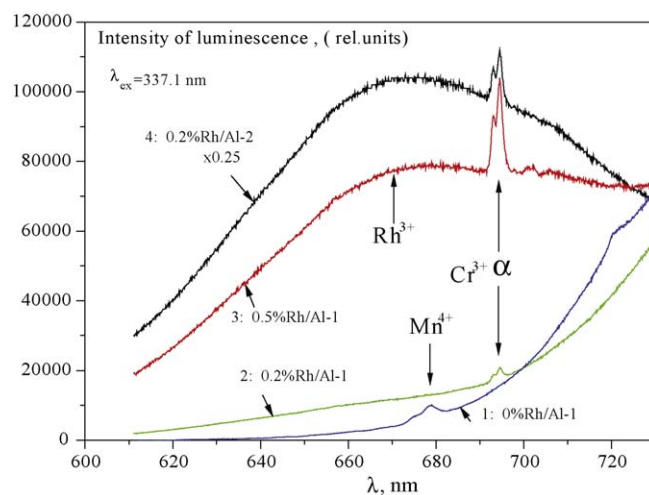


Fig. 7. LIL spectra of 0% Rh/Al-1 (1), 0.2% Rh/Al-1 (2), 0.5% Rh/Al-1 (3), and 0.2% Rh/Al-2 (4) under excitation wavelength $\lambda_{ex} = 337.1$ nm calcined under the same conditions (1000 °C, 20 h).

Cr^{3+} ions may characterize the bulk corundum concentration in the sample.

The data obtained by LIL and XRD for the 0.1 wt.% Rh/Al-2 series are compared in Table 2. These data show a good correlation between the corundum concentration and the intensities of the LIL bands of Cr^{3+} and Rh^{3+} ions stabilized in this phase. The maximum concentration of these ions is achieved after calcination at 1200 °C for 20 h. Longer calcination does substantially change the intensity of these lines.

The presented data led us to two important conclusions. First, the LIL spectra of uniformly distributed in alumina acceptor Cr^{3+} ions under excitation with wavelength $\lambda_{\text{ex}} = 337.1$ nm for Rh/Al₂O₃ samples via FRET mechanism reflects the actual fraction of the corundum phase in alumina in the vicinity of donor ions $\text{Rh}^{3+}/\alpha\text{-Al}_2\text{O}_3$. Taking into account the high-LIL sensitivity to narrow R_α doublet, these impurity ions can be used as a probe of the Rh^{3+} ions incorporated in the bulk of forming corundum phase starting from concentrations as low as $10^{-3}\%$, i.e. from the earliest stages.

Second, the concentration of Rh^{3+} ions in corundum determined by the LIL method correlates with the $\alpha\text{-Al}_2\text{O}_3$ concentration in the sample. This means that corundum is formed in the Al₂O₃ sample with Rh^{3+} ions fairly homogeneously dissolved in the low-temperature $\delta\text{-Al}_2\text{O}_3$ phase. It is important that the average concentration of these ions does not change when the $\alpha\text{-Al}_2\text{O}_3$ phase is formed after calcination at 1000 °C.

Thus, there is no doubt that Rh^{3+} and Cr^{3+} ions initially dissolved in the low-temperature alumina phases are incorporated into the regular corundum structure. Theoretically, there are two methods for Rh^{3+} incorporation in corundum. The first one is direct diffusion of Rh^{3+} ions to the formed corundum phase. In our opinion, such diffusion is rather unlikely at moderate temperatures, such as 1000 °C. The other option is Rh incorporation during the formation of the $\alpha\text{-Al}_2\text{O}_3$ phase. Most likely, this is the way Rh is incorporated in corundum in our system. In this case, Rh^{3+} ions dissolved in the $\delta\text{-Al}_2\text{O}_3$ phase are captured by the forming corundum structure and stabilized in it. Meanwhile, the average bulk concentration of Rh^{3+} ions does not change. As a result, the intensity of their LIL spectrum reflects the corundum concentration in the samples (Table 2).

Fig. 7 presents the LIL spectra of the catalysts with different Rh concentrations prepared using the thermally stable support Al-1 (spectra 1–3) and 0.2% Rh/Al-2 catalyst prepared using the support with lower thermal stability (spectrum 4) after calcination under similar conditions (1000 °C, 20 h). The characteristic band attributed to Rh^{3+} ions in corundum is higher when the Rh loadings in the sample is higher and also observed in the LIL spectra of Rh/Al-2 catalysts. However, its intensity is much higher than in the case of Rh/Al-1 catalysts because the corundum concentration in the former case is much higher.

The incorporation of Rh ions in the bulk of the forming corundum phase is observed at Rh concentrations as low as 0.01 wt.% (Fig. 8). As noted above, at such Rh concentrations the

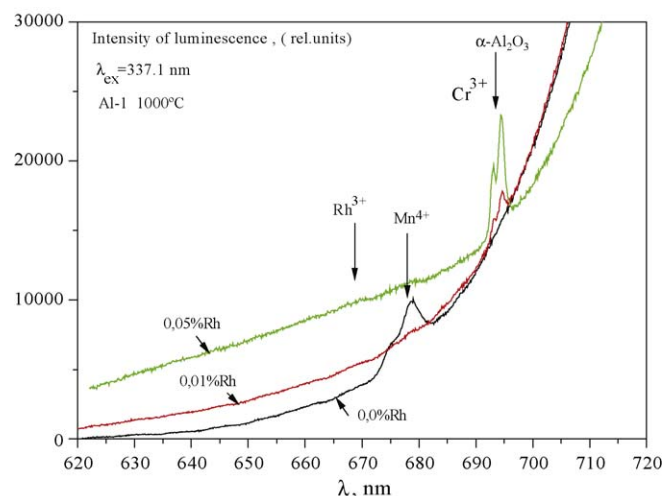


Fig. 8. LIL spectra of 0% Rh/Al-1 (1), 0.01% Rh/Al-1 (2), 0.05% Rh/Al-1 (3) calcined under the same conditions (1000 °C, 20 h). The arrows mark the positions of the characteristic band of Rh^{3+} and lines of Cr^{3+} ions in corundum and Mn^{4+} ions in $\alpha\text{-Al}_2\text{O}_3$.

luminescence intensity of R_α line of Cr^{3+} ions does not reflect the total corundum concentration in the sample. It rather correlates with the concentration of corundum where Rh^{3+} and Cr^{3+} ions are located close to each other ($r < 8$ nm).

The above results point to the possibility of initializing phase transformations promoted by Rh ions at the earliest stages of the formation of α -alumina phases.

As noted earlier, diffusion of Rh ions in corundum at ca. 1000 °C is quite unlikely. Nevertheless, to determine its role in the processes under consideration, we performed special experiments. Rh (0.5 wt.%) was deposited by a standard procedure on the corundum phase preliminary prepared by calcination of the Al-2 sample at 1200 °C ($\text{SSA} \sim 0.5 \text{ m}^2/\text{g}$). Then the sample was subjected to standard calcination at 1000 °C for 20 h. The luminescence spectra of such samples do not contain the band with $\lambda = 670\text{--}680$ nm from Rh^{3+} ions in corundum. Taking into account high sensitivity of the method, this indicates very low concentration of such ions. This result shows also that diffusion of Rh^{3+} ions in corundum at the experimental temperature can be neglected.

Thus, it can be concluded that the incorporation of Rh^{3+} ions in corundum observed in the experiment is irreversible and occurs during its formation from the Rh^{3+} ions dissolved quite uniformly in the bulk of the low-temperature polymorphic modifications of alumina. More detailed analysis of the specific features of Rh migration during the formation of the corundum phase and their possible promoting effect on this process using LIL spectroscopy with excitation with two lines $\lambda_{\text{ex}} = 337.1$ nm (FRET) and $\lambda_{\text{ex}} = 514.5$ nm (region of intrinsic absorption ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ of Cr^{3+} ions) will be the subject of our later publication.

4. Conclusions

The combination of the catalytic ethane hydrogenolysis and LIL spectroscopy allowed us to study Rh diffusion from the surface to the bulk of Rh/Al₂O₃ catalysts, stabilization of Rh ions in the corundum phase formed during calcination under oxidizing conditions and observe the incorporation of Rh^{3+} ions in corundum and possible promoting effect at the earliest stages of the formation of α -phases at Rh concentrations as low as 0.01%.

Our experiments showed that the thermal treatment at temperatures exceeding 800 °C results in active Rh migration from the surface to the bulk of the support eventually leading to relatively uniform Rh distribution in the alumina phase. Meanwhile, the

Table 2

Relative intensities of luminescence bands in LIL spectra attributed to Rh^{3+} ($\lambda = 670\text{--}680$ nm) and Cr^{3+} ($\lambda = 694$ nm) under excitation with wavelength $\lambda_{\text{ex}} = 337.1$ nm and XRD data on the phase composition of 0.1% Rh/Al-2 catalyst calcined at different temperatures for 20 h.

T (°C)	LIL(Rh^{3+})	LIL(Cr^{3+})	XRD data (%)		
			α	δ	γ
550	–	–	–	–	100
840	0.08	0.05	–	30	70
1000	9.9	7.5	10	90	–
1200 ^a	100	100	100	–	–

^a The intensities of the LIL spectra of Rh^{3+} and Cr^{3+} ions in these samples were taken as 100%. This intensity does not increase after longer calcination at 1200 °C.

surface Rh concentration decreases by more than an order of magnitude. Further increase of the calcination temperature does not have a major effect on the surface Rh concentration.

For the catalysts with low-thermal stability of the alumina support, Rh^{3+} ions dissolved in the low-temperature alumina phase are captured by the corundum phase growing during the thermal treatment and are stabilized inside it. This process is irreversible. Rhodium ions trapped inside the corundum phase cannot go back on the surface in the studied temperature range. Thus, the stability of alumina support with respect to its transformations to corundum is one of the important factors accounting for irreversible deactivation of $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts.

Acknowledgment

This work was partly supported by the Russian Foundation for Basic Research (grant 07-03-12149).

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